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METHOD FOR PRODUCING MIXTURES OF LOW-FOAMING NON-IONIC SURFACTANTS WITH
AN ACETAL STRUCTURE
[Verfahren zur Herstellung von Gemischen schaumarmen nicht-ionischer
Tenside mit Acetalstruktur]

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OF LOW-FOAMING NON-IONIC
SURFACTANTS WITH AN ACETAL
STRUCTURE

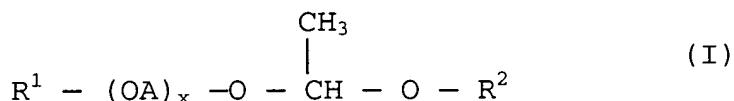
FOREIGN TITLE [54A] : VERFAHREN ZUR HERSTELLUNG VON
GEMISCHEN SCHAUMARMER
NICHT-IONISCHER TENSIDE MIT
ACETALSTRUKTUR

Description

/1*

The present invention relates to an improved method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure which

A) contain 70 to 99 wt.% of one or several asymmetrical acetals of the general formula I



in which

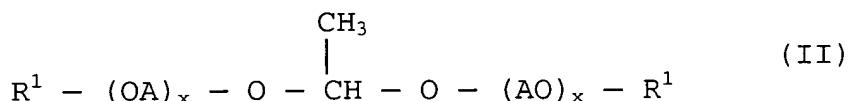
R^1 signifies a C_1 to C_{30} alkyl residue, a C_3 to C_{30} alkenyl residue, or a C_7 to C_{30} aralkyl residue, or alkaryl residue,

R^2 means a C_1 to C_{10} alkyl residue,

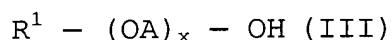
A stands for a 1,2-alkylene group with 2 to 4 C atoms, and

x may assume values from 1 to 50, and

B) 1 to 30 wt.% of one or several symmetrical acetals of the general formula II



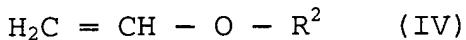
in which the variables R^1 , A , and x , have the above-specified meanings, through a conversion of alkoxylates of the general formula III



with vinyl ethers of the general formula IV

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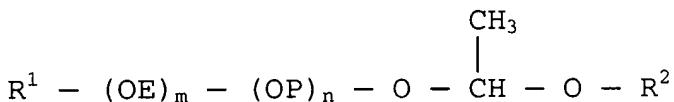


in the presence of acids as catalysts.

Because a part of these surfactant mixtures represents new substances, the present invention also relates to these new mixtures.

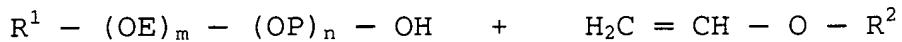
Nowadays, washing and cleaning processes in industrial settings, commercial enterprises, and domestic households increasingly require surface-active substances which, on the one hand, distinguish themselves through alkali stability, low-foaming properties, and effective anti-froth characteristics, and, on the other hand, through rapid and total biodegradability.

In the search for compounds which meet these requirements, alkyl alkoxylates with an acetal structure have been proposed; for instance, DE-A 2252186 (1) proposes compounds of the type

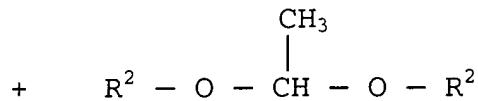
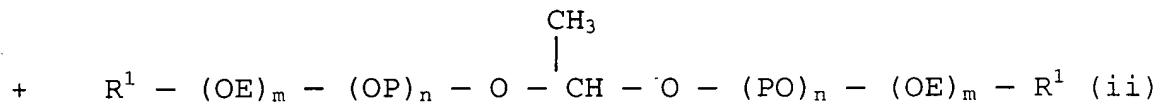
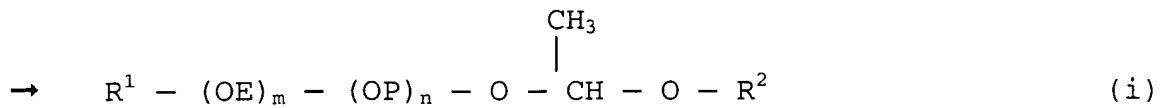


whereas R^1 signifies a long-chained, saturated, or unsaturated alkyl residue, or an alkyl aryl residue, E means ethylene, and P means propylene, m and n may be a number from 1 to 30 or 5 to 50, R^2 represents a shorter alkyl chain with 1 to 10 carbon atoms, or a residue with the formula $\text{R}^1 - (\text{EO})_m - (\text{PO})_n$.

In the above laid-open specifications, the preparation of these types of acetals is described under catalysis of strong protonic acids or Lewis acids, whereas it is mentioned that a variety of products are obtained by varying the temperature:



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Thus, at temperatures < 30°C, product (i) is, preferably, formed while at temperatures > 30°C, product (ii) is formed with increasing temperatures.

US-A 3244753 (2) relates to the conversion of alkyl alkoxylates with vinyl ethers under catalysis of strong protonic acids and with the addition of phosphorus-containing acids for the purpose of realizing a color-brightening effect; however, the conversion is only quantified via the OH number, and a product composition of the various acetals is not specified.

In Example 1 of this US patent document, the preparation of the compound

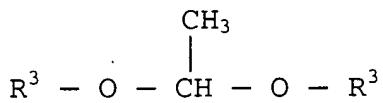


is described through a conversion of oxethylated tridecyl alcohol with n-butyl vinyl ether in the presence of catalytic quantities of p-toluene sulfonic acid and hydrophosphoric acid at 35 to 40°C; in this process, the acetal is obtained in a bright color in a yield of 94%.

Therefore, it was the objective of the present invention to provide an economical and simple method in which the transacetalization of the compound I into compound II is largely avoided, compound I is obtained in high yields, and a bright-colored product is produced. This objective is based on the fact that Type I compounds exhibit substantially improved biodegradability over Type II compounds.

Moreover, it is desirable for economic reasons, to only use a /4 catalyst which, at the same time, controls the conversion in the desired sense while delivering a bright-colored product.

Accordingly, the method defined at the beginning of the text was found in the presence of protonic acids or Lewis acids as catalysts which is characterized in that, the conversion is carried out in the presence of one or several acetal aldehyde dialkyl acetals of the general Formula V



in the quantity from 0.1 to 20 mol of the compounds V per mol III, in which R³ signifies a C₁ to C₁₀ alkyl residue, whereas R² and R³ may have the same or different meanings.

Surprisingly, it was found that, by adding the compounds V, which, practically, serve as a solvent in this process, the yield of the desired products I can be increased substantially. On the other hand, what is realized through this, is that, during the exothermic reaction, the reaction temperatures can be increased from about 20°C to > 30°C, and,

thus, an elaborate, energetically unfavorable cooling of the reaction mixture can be avoided in the operational realization.

The acetaldehyde dialkyl acetals V which are used as solvents and reaction partners can easily be prepared from the appropriate alkyl vinyl ether and the alkyl alcohol under acid catalysis at 50 to 100°C. During this preparation - due to the homogeneous alkyl vinyl ethers - the problem of transacetalization and, hence, the preparation of a product mixture, does not occur. During this conversion, the acetaldehyde dialkyl acetals V are created nearly quantitatively and are obtained in yields > 95% after the neutralization and distillation. After the conversion, the acetaldehyde dialkyl acetals V which are used in the acetalization of the alkoxylates III into the products I, can easily be separated off and reused in several synthesis cycles without a problem. This is an essential advantage compared to an excess of alkyl vinyl ethers, as it is proposed in (1) because this vinyl ether surplus cannot be unquestionably reused - due to contaminations, e.g., acetal formations.

The cyclic, or, preferably, acyclic alkyl residues R³ of the /5 acetaldehyde dialkyl acetals V may contain 1 to 10, preferably, 1 to 4 C atoms. In specific, branched C₃ or C₄ alkyl residues are options for this; the isobutyl residue is particularly appropriate. Those acetaldehyde dialkyl acetals V in which R³ has the same meaning as R², i.e., like the alkyl residue in the vinyl ethers IV, are also preferred.

The use of acetaldehyde dialkyl acetals V has the advantage that the reaction temperature of the conversion of III can be increased with

IV to 30 to 80°C, preferably, 35 to 70°C, most specifically, 40 to 60°C.

On the one hand, this has the result that a cost-intensive cooling is eliminated in the management of the reaction, and, on the other hand, potential viscosity problems, as they particularly occur at temperatures < 30°C, are avoided in the reaction without solvents.

In a preferred embodiment of the method, the acetaldehyde dialkyl acetal V is presented in the reaction vessel, and, at the same time, vinyl ethers IV, and, separately, a mixture of alkoxylate III, and a catalyst, are metered in. In this process, the vinyl ether IV's immediate reaction with the alcohol into the desired product I is guaranteed and, therefore, unnecessary damages to the color of the product are avoided that would be created due to a local excess of the vinyl ether in the presence of a strong acid concentration through polymerization reactions.

The molar ratio of acetaldehyde dialkyl acetal V relative to the alkoxylate III is 0.1:1 to 20:1, preferably, 0.5:1 to 10:1. If no mixtures are desired with regard to the alkyl chain, which is preferable, the alkyl residue R³ in V must, of course, be identical with the alkyl residue R² of the alkyl vinyl ether III which is used. However, if mixtures with regard to this alkyl residue are options and desired, acetaldehyde dialkyl acetals V and alkyl vinyl ethers III with various alkyl residues may also be used. Alkoxylate III and alkyl vinyl ether IV are usually used equimolar or nearly equimolar. A vinyl ether excess IV is not required to realize high contents of I.

Moreover, the process defined at the beginning of the text was found in the presence of protonic acids as catalysts which is characterized in that, organic acids with a pK_s value of 1 to 7 are used as catalysts in relation to the first dissociation step of the acids in water.

Surprisingly, it was found that, by using such mild organic acids /6 in the conversion of alkoxylates III with alkyl vinyl ethers IV, the transacetalization can largely be suppressed under formation of the symmetrical acetals II, and the asymmetrical acetals I are available in high yields. Moreover, it surprisingly was found that the reaction can be carried out at higher temperatures than the conversion with strong organic acids, mineral- or Lewis acids. This has the result that a solvent which practically must be added at temperatures $< 30^\circ\text{C}$ due to the often increased viscosity, can be dispensed with. In addition, strong discolorations of the product, as they easily occur with strong mineral-Lewis-, or strong organic acids at elevated temperatures ($> 50^\circ\text{C}$), are no longer observed.

The mild organic acids that are used, which may contain additional functional groups, such as hydroxyl, carbonyl, nitrile groups, olefinic double bonds, aryl residues, or halogen atoms, are acids with pK_s values of 1 to 7, preferably, 1.2 to 5, particularly, 1.5 to 4, relative to the first dissociation step of the acids in water. Specifically, these organic acids are carboxylic acids. The following can be mentioned as examples: oxalic acid, citric acid, nitrilotriacetic acid, tartaric acid, fumaric acid, terephthalic acid, malic acid, propionic acid, salicylic acid,

succinic acid, glutaric acid, adipinic acid, acrylic acid, methacrylic acid, lactic acid, phthalic acid, malonic acid, benzoic acid, acetic acid, formic acid, α -halogen carboxylic acids, e.g., chloroacetic acid or dichloroacetic acid, propionic acid, citraconic acid, and maleic acid.

Of these, formic acid, acetic acid, oxalic acid, citric acid, tartaric acid, phthalic acid, terephthalic acid, fumaric acid, and, particularly, maleic acid, are preferred.

As a rule, the catalysts are neutralized after the completed conversion with a standard base.

To realize the desired effects, particularly, the production of bright-colored products, no additional catalyst component, other than the mentioned mild organic acids, is necessary.

In this process, the catalyst concentration is in the range that is normally used and, as a rule, it is 0.1 to 10 mol%, preferably, 0.3 to 7 mol%, particularly, 0.5 to 5 mol%, relative to the vinyl ether VI that is used.

If the mentioned mild, organic acids are used, the conversion /7 temperature, normally is 50 to 150°C, preferably, 60 to 130°C, particularly, 70 to 100°C.

As a rule, the reaction is carried out in such a way that the vinyl ether component is presented in the reaction vessel and mixed with the mild, organic acids as the acidic catalyst. Then, heating occurs to the conversion temperature, and the alkoxylate component is metered in. In most cases, more agitation periods from 0.25 to 20 h follow depending

upon the strength of the acid and acid concentration of the catalyst that is used. However, as a rule, only agitation periods from 0.25 to 5 h are needed, with the preferred use of maleic acid, 0.25 to 1 h is required.

The management of the reaction may also be carried out inversely, i.e., by presenting the alkoxylate or alkoxylate/catalyst mixture and metering in the vinyl ether/catalyst mixture or vinyl ether. The alkoxylate component and the vinyl ether component are usually used equimolar or nearly equimolar. A vinyl ether excess is not required for the realization of high asymmetrical acetal I contents.

The following are mentioned as examples of straight-chained or branched alkyl and alkenyl residues R¹: n-hexyl, n-heptyl, n-octyl, 2-ethyl hexyl, n-nonyl, isononyl, n-decyl, isodecyl, n-undecyl, n-dodecyl, n-tridecyl, isotridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-octadecyl, n-eicosyl, oleyl, linolyl, and linolenyl. The residues R¹, preferably, are straight-chained or only branched to a slight extent, i.e., they contain a maximum of 3-methyl or ethyl side chains.

Depending upon the origin of the alcohol which is used in the synthesis, R¹ are residues of naturally occurring fatty alcohols, or, preferably, of synthetically produced oxo- or Ziegler alcohols. Examples of alcohols which may well be used and which are prepared with oxosynthesis are C₁₀, C₁₃, and C₁₅ alcohols, as well as C₉/C₁₁, C₁₀/C₁₂, C₁₂/C₁₄, C₁₃/C₁₅, and C₁₆/C₁₈ alkanol mixtures. Examples of alcohols in accordance with the Ziegler synthesis, which may well be used, are C₈/C₁₀, C₁₀/C₁₂, C₁₂/C₁₄, C₁₂/C₁₆, C₁₆/C₁₈, and C₁₆/C₂₀ alkanol mixtures.

Because, as a rule, the alcohols which are used in the synthesis represent statistical homologen and also isomer mixtures, it is expedient to speak of an average number of C atoms in the residues R¹.

For R¹, alkyl or alkenyl residues with 8 to 20 C atoms, /8 particularly, with 10 to 18 C atoms, are preferred. Those residues R¹ which can be traced back to the C₁₀ fraction, the C₁₃ fraction, the C₁₀/C₁₂, C₁₂/C₁₄, C₁₃/C₁₅, or C₁₆/C₁₈ fraction of an alcohol obtained in accordance with oxosynthesis are particularly advantageous.

The variable R¹ may also stand for aralkyl residues, particularly, phenyl alkyl residues, or alkaryl residues, particularly, alkyl phenyl residues, preferably, with a total of 8 to 20 C atoms, respectively.

Pertinent examples include: benzyl, β-phenyl ethyl, 4-phenyl butyl, ω-phenyl decyl, ω-phenyl dodecyl, o-, m-, or p-toluene, o-, m-, or p-ethyl phenyl, o-, m-, or p-butyl phenyl, p-decyl phenyl, or p-dodecyl phenyl.

In particular, the 1,2-alkylene groups A signify the ethylene group, but, apart from it, also the propylene-, 1,2-butylene- and 2,3-butylene groups. Every group A may also signify a statistical mixture of several of the mentioned 1,2-alkylene groups, or a group which is built from up to three unitary blocks of these alkylene groups; however, 1,2-alkylene groups containing only one building unit are preferred.

Preferably, the degree of alkoxylation x is 2 to 15, particularly, 3 to 12, whereas these numbers are to be viewed as average values for statistical distributions of alkoxylation products.

The cyclic, or, preferably, acyclic alkyl residues R² of the vinyl ethers IV which are used may contain 1 to 10, preferably, 1 to 4 C atoms.

Specifically, branched C₃ or C₄ alkyl residues are options for this, the isobutyl residue being particularly appropriate.

Lewis acids, e.g., BF₃, SbCl₅, or TiCl₄, strong mineral acids, e.g., hydrochloric acid (especially in an anhydrous form as hydrogen chloride), sulfuric acid, or phosphoric acid, or strong organic acids, e.g., trifluoromethane sulfonic acid, methane sulfonic acid, trifluoroacetic acid, dodecyl benzene sulfonic acids, or toluene sulfonic acids, are appropriate as catalysts for the conversion of III with IV.

Of these, hydrochloric acid, sulfuric acid, phosphoric acid, methane sulfonic acid, benzene sulfonic acid, p-dodecyl benzene sulfonic acid, and, particularly, p-toluene sulfonic acid, are preferred. These catalysts are employed in the standard quantities for this purpose. To realize the desired effects, particularly, the production of bright-colored products, no additional catalyst component is required. /9

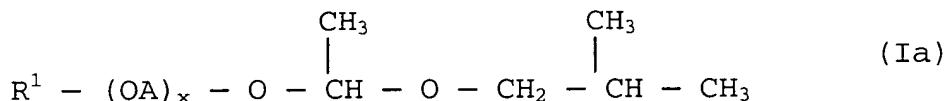
As a rule, the catalysts are neutralized with a conventional base after the conversion has taken place.

The reaction management in accordance with the invention results in product mixtures which, preferably, contain the asymmetrical acetal I. Preferably, these product mixtures contain 75 to 98 wt.% of the compounds I, and 2 to 25 wt.% of the compounds II, above all, 80 to 95 wt.% of I, and 5 to 20 wt.% of II, particularly, 83 to 92 wt.% of I, and 8 to 17 wt.% of II, with the use of the acetaldehyde dialkyl acetals,

or 82 to 94 wt.% of I and 6 to 18 wt.% of II, when mild organic acids are used as catalysts. Apart from this, for instance, small quantities of acetaldehyde dialkyl acetals which are created during the transacetalization from I to II, may be present. The predominance of I results in an improved biodegradability of the products. At the same time, the products are alkali-stable, low-foaming, and particularly appropriate for cleaning processes with high mechanical stress, e.g., automatic dishwashing, or commercial bottle washing.

Mixtures of low-foaming, non-ionic surfactants with an acetal structure which contain

A) 70 to 99 wt.% of one or several asymmetrical acetals of the general Formula Ia

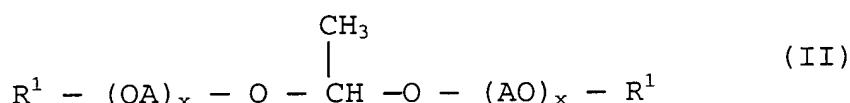


in which

R^1 signifies a C_1 to C_{30} alkyl residue, a C_3 to C_{30} alkenyl residue, or a C_7 to C_{30} aralkyl residue, or alkaryl residue,

A stands for a 1,2-alkylene group with 2 to 4 C atoms, and x may assume values from 1 to 50, and

B) 1 to 30 wt.% of one or several symmetrical acetals of the general formula II



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in which the variables R¹, A, and x, have the above-specified meanings are also a subject of the invention.

These mixtures exhibit particularly advantageous application-technical properties.

The following examples shall describe the method in accordance with the invention in greater detail.

Preparation of acetaldehyde diisobutyl acetal

37 g (0.5 mol) of iso-butanol were presented in a flask and mixed with 0.657 g (0.003 mol) of p-toluene sulfonic acid. It was heated to 60°C and 50 g (0.5 mol) of vinyl isobutyl ether were added under agitation within 1 h. After that, we continued agitating for 30 min at 60°C, neutralized with Na₂CO₃, filtrated, and distilled under normal pressure. The yield was 84 g (96.9%).

Example 1

200 g of acetaldehyde diisobutyl acetal were presented in a flask and heated to 40°C under agitation. 4.9 g of p-toluene sulfonic acid with 326 g (0.5 mol) of fatty alcohol ethoxylate (C₁₂-C₁₈ fatty alcohol mixture converted with 10 mol of ethylene oxide) were mixed separately.

At the same time, 50 g (0.5 mol) of vinyl isobutyl ether and the fatty alcohol ethoxylate/catalyst mixture were metered into the flask within 2 h. After the metering was completed, we continued agitation for 30 min, neutralized with Na₂CO₃, filtrated, and largely distilled off the excess acetaldehyde diisobutyl acetate under a water jet vacuum. 380

g of a clear, colorless product were obtained. The composition - also of the additional examples - is provided in the following Table 1.

Examples 2 and 3

Analogue to Example 1, 100 g or 300 g of acetaldehyde diisobutyl acetal were used.

Comparison Example A

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50 g (0.5 mol) of vinyl isobutyl ether were presented in the flask, heated to 40°C, and the fatty alcohol ethoxylate/catalyst mixture described in Example 1 was metered in within 2 h. After agitation for 30 min, neutralization, and filtration, a product of dark brown color was obtained.

Comparison Example B

At the same time, 50 g (0.5 mol) of vinyl isobutyl ether and the fatty alcohol ethoxylate/catalyst mixture described in Example 1 were dripped in. In this process, for technical reasons, an effective agitation could not be carried out until after 10% of the 2-hour metering period. The workup was carried out analogue to Example 1.

Comparison Example C

The fatty alcohol ethoxylate/catalyst mixture described in Example 1 was presented in the flask and vinyl butyl ether was added in drops within 2 h. The workup was carried out analogue to Example 1.

Comparison Example D

100 g of methyl tert. butyl ether were presented in the flask, mixed with 50 g (0.5 mol) of vinyl isobutyl ether, and left at 20°C. The fatty alcohol ethoxylate/catalyst mixture was metered into this mixture within 2 h. The workup was carried out analogue to Example 1.

Comparison Example E

Example D was repeated at 40°C.

Comparison Example F

100 g of methyl tert. butyl ether were mixed with 4.9 g of p-toluene sulfonic acid and left at 20°C. Separately and at the same time, the fatty alcohol ethoxylate and vinyl isobutyl ether were metered in within 2 h. The workup was carried out analogue to Example 1.

Comparison Example G

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Analogue to Example 1, the appropriate amounts of acetaldehyde diisobutyl acetal, isobutyl vinyl ether, and p-toluene sulfonic acid were presented in the flask at 20°C, and the fatty alcohol ethoxylate was metered in. During the metering process, an increasing discoloration of the product was observed. This was also observed when acetaldehyde diisobutyl acetal was left out as the solvent.

Comparison Example H

Analogue to Example 1, the appropriate amounts of acetaldehyde diisobutyl acetal and p-toluene sulfonic acid were presented at 20°C, and, separately, but simultaneously, the appropriate amounts of fatty

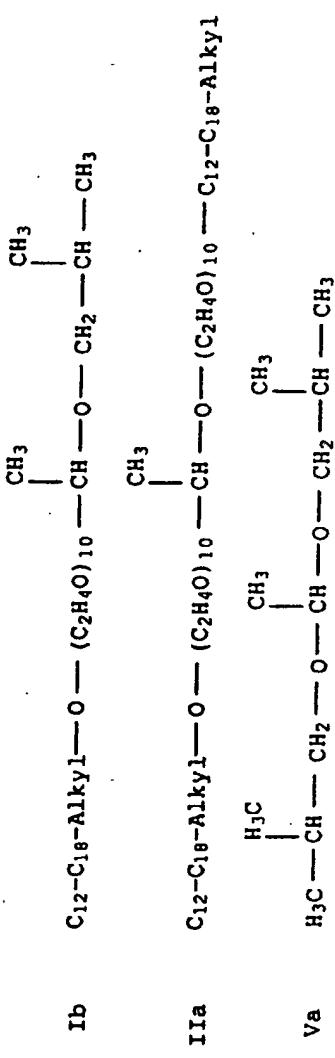
alcohol ethoxylate and vinyl isobutyl ether were metered in. A strong discoloration of the product was observed during the metering process.

Table 1

Compositions and Results

Beispiel Nr.	Temperatur [°C]	OH-Zahl [mg KOH/g]	Ib [Gew.-%]	IIIa [Gew.-%]	Va [Gew.-%]	Farbe
1	40	4,7	88,5	10,0	1,5	farblos
2	40	5,4	89,8	8,4	1,8	farblos
3	40	3,8	85,1	12,1	2,8	farblos
A	40	6,5	54,8	37,3	7,8	dunkelbraun
B	40	5,5	65,0	29,2	5,8	gelb
C	40	6,6	53,5	37,5	9,0	gelb
D	20	6,4	78,0	20,3	1,7	hellgelb
E	40	6,1	61,3	35,0	3,7	gelb
F	20	6,4	67,3	27,7	5,1	dunkelbraun
G	20	6,0	77,2	18,2	4,5	dunkelbraun
H	20	6,3	79,7	17,0	3,1	dunkelbraun

Component Structures:



Key:

Beispiel Nr. = Example No.

Temperatur ($^{\circ}$ C) = temperature ($^{\circ}$ C)

OH-Zahl [mg KOH/g] = OH number [mg KOH/g]

Ib (Gew. %) = Ib (wt.%)

IIa (Gew. %) = IIa (wt.%)

Va (Gew. %) = Va (wt.%)

Farbe = color

farblos = colorless

dunkelbraun = dark brown

gelb = yellow

hellgelb = bright yellow

Example 4

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75 g (0.75 mol) of vinyl isobutyl ether were presented in a flask and mixed with 4 g (0.035 mol) of maleic acid. The mixture was heated to 70 $^{\circ}$ C. Under vigorous agitation, 480 g (0.75 mol) of an addition product from a C₁₂-C₁₈ fatty alcohol mixture with 9.5 mol of ethylene oxide (OH number 89 mg KOH/g) were metered in within 1 h, whereas the temperature was increased to 80 $^{\circ}$ C. After the metering process had been completed, we continued agitation for an additional 30 min at 80 $^{\circ}$ C, neutralized, and filtrated. After removing highly volatile components under a water jet vacuum, 542 g of a limpid, bright-colored product was obtained, the composition of which is provided in the following Table.

Examples 5 to 9

Analogue to Example 4, the additional organic acids which are provided in the following Table 2, could also be used as catalysts. In every case, limpid, colorless products were obtained, the compositions of which can be deduced from the following Table.

Comparison Examples J and E

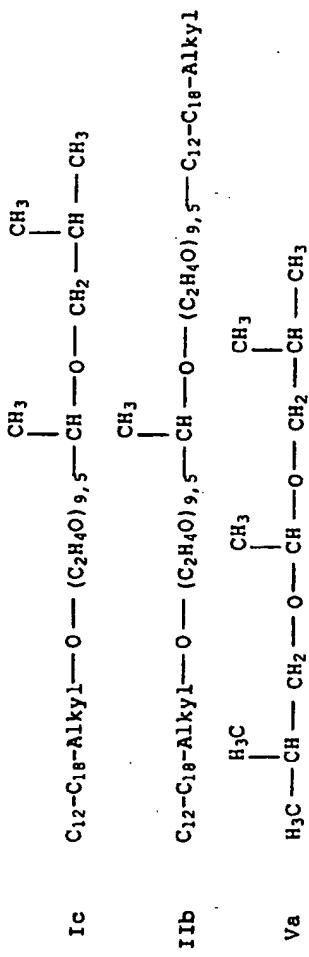
Analogue to Example 4, 3.8 g (0.02 mol) of p-toluene sulfonic acid or 1.96 g (0.02 mol) of phosphoric acid were used. After neutralization, the products were colored dark brown to black.

Table 2

Compositions and Conversion Parameters

Beispiel Nr.	Katalysator	(pK _s -Wert)	Umsetzungstemperatur [°C]	Nachführzeit [h]	*Verbindung [Gew.-%]
4	Maleinsäure	(1,83)	80	1,0	Ib IIa V
5	Citronensäure	(3,08)	94	10,0	88,9 93,7 5,5
6	Oxalsäure	(1,23)	85	0,25	82,2 13,3 4,4
7	D,L-Weinsäure	(2,98)	94	6,5	91,1 7,7 1,2
8	Ameisensäure	(3,75)	94	7,0	93,0 5,8 1,1
9	Essigsäure	(4,75)	94	9,0	92,2 6,0 1,8
J	p-Toluolsulfonsäure	(-6,5)	70	0,25	54,2 37,0 8,8
K	Phosphorsäure	(2,15)	90	0,25	49,8 39,7 10,4

Component Structures:



Key:

Beispiel Nr. = Example No.

Katalysator (pK_s-Wert) = catalyst (pK_s value)

Umsetzungstemperatur = conversion temperature

Nachrührzeit = agitation time

*Verbindung (Gew. %) = * compound (wt. %)

Maleinsäure = maleic acid

Citronensäure = citric acid

Oxalsäure = oxalic acid

D, L-Weinsäure = D, L-tartaric acid

Ameisensäure = formic acid

Essigsäure = acetic acid

p-Toluolsulfonsäure = p-toluene sulfonic acid

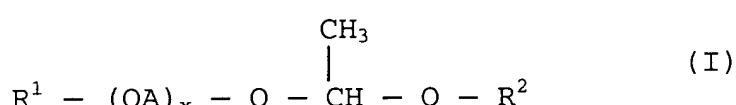
Phosphorsäure = phosphoric acid

Patent Claims

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1. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure, containing

A) 70 to 99 wt.% of one or several asymmetrical acetals of the general formula I



in which

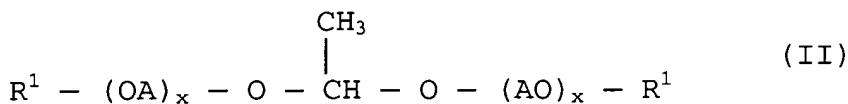
R¹ signifies a C₁ to C₃₀ alkyl residue, a C₃ to C₃₀ alkenyl residue, or a C₇ to C₃₀ aralkyl residue, or alkaryl residue,

R² means a C₁ to C₁₀ alkyl residue,

A stands for a 1,2-alkylene group with 2 to 4 C atoms, and

x may assume values from 1 to 50, and

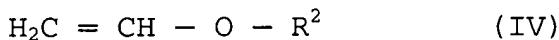
B) 1 to 30 wt.% of one or several symmetrical acetals of the general formula II



in which the variables R^1 , A, and x, have the above-specified meanings, through a conversion of alkoxylates of the general formula III

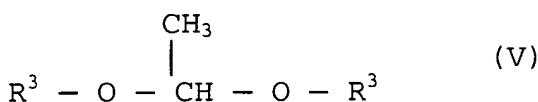


with vinyl ethers of the general formula IV



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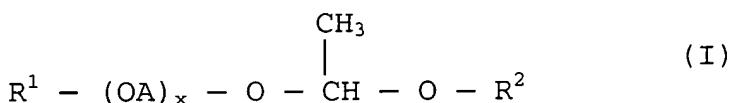
in the presence of protonic acids or Lewis acids as catalysts, characterized in that the conversion is carried out in the presence of one or several acetaldehyde dialkyl acetals of the general Formula V



in which R^3 signifies a C_1 to C_{10} alkyl residue, whereas R^2 and R^3 may have the same or different meanings, in a quantity of 0.1 to 20 mol of the compounds V per mol of III.

2. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure, containing

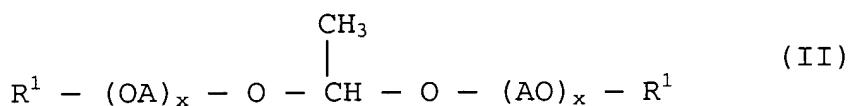
A) 70 to 99 wt.% of one or several asymmetrical acetals of the general Formula I



in which

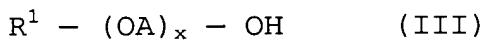
R^1 signifies a C_1 to C_{30} alkyl residue, a C_3 to C_{30} alkenyl residue, or a C_7 to C_{30} aralkyl residue, or alkaryl residue,

R^2 means a C_1 to C_{10} alkyl residue,
A stands for a 1,2-alkylene group with 2 to 4 C atoms, and
x may assume values from 1 to 50, and
B) 1 to 30 wt.% of one or several symmetrical acetals of the general formula II



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in which the variables R^1 , A, and x, have the above-specified meanings, through a conversion of alkoxylates of the general formula III



with vinyl ethers of the general formula IV



in the presence of protonic acids as catalysts, characterized in that organic acids with a pK_s value of 1 to 7 is used as the catalyst, relative to the first dissociation step of the acids in water.

3. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure in accordance with Claim 1 or 2, containing

- A) 80 to 95 wt.% of compounds I, and
- B) 5 to 20 wt.% of compounds II.

4. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure in accordance with Claims 1 to 3, whereas the variable R^1 in the compounds I and II signifies a C_8 to C_{20} alkenyl residue.

5. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure in accordance with Claims 1 to 4, whereas the variable R² in the compounds I means a branched C₃ or C₄ alkyl residue.

6. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure in accordance with Claims 1 to 5, whereas the variable A stands for an ethylene group, and the variable x may assume values from 2 to 15.

7. Method for the preparation of mixtures of low-foaming, non- /19 ionic surfactants with an acetal structure in accordance with Claim 1, characterized in that those acetaldehyde dialkyl acetals V are used in which the variable R³ has the same meaning as R².

8. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure in accordance with Claim 1 or Claim 7, with the use of hydrochloric acid, sulfuric acid, phosphoric acid, methane sulfonic acid, benzene sulfonic acid, p-toluene sulfonic acid, or p-dodecyl benzene sulfonic acid, as the catalyst.

9. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure in accordance with Claims 1, 7, or 8 through conversion at a temperature from 30 to 100°C.

10. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure in accordance with Claims 1, 7, or 9, characterized in that the acetaldehyde dialkyl acetal V is presented

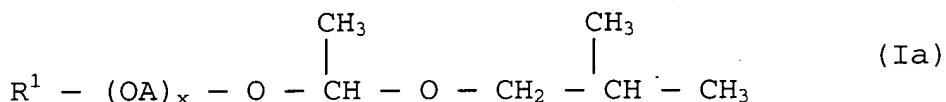
in the reaction vessel and vinyl ether IV, as well as a mixture of alkoxylate III and a catalyst are metered in at the same time.

11. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure in accordance with Claim 2, characterized in that, formic acid, acetic acid, oxalic acid, citric acid, tartaric acid, phthalic acid, terephthalic acid, fumaric acid, or maleic acid, are used.

12. Method for the preparation of mixtures of low-foaming, non-ionic surfactants with an acetal structure in accordance with Claim 2 or 11 at a temperature from 50 to 150°C.

13. Mixtures of low-foaming, non-ionic surfactants with an acetal structure, containing

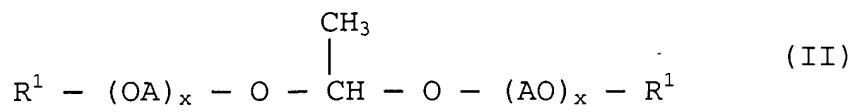
A) 70 to 99 wt.% of one or several asymmetrical acetals of the general Formula Ia



in which

R¹ signifies a C₁ to C₃₀ alkyl residue, a C₃ to C₃₀ alkenyl residue, or a C₇ to C₃₀ aralkyl residue, or alkaryl residue, /20
A stands for a 1,2-alkylene group with 2 to 4 C atoms, and
x may assume values from 1 to 50, and

B) 1 to 30 wt.% of one or several symmetrical acetals of the general formula II



in which the variables R^1 , A, and x, have the above-specified meanings.